



Catalytic epoxidation of alkenes with 30% H₂O₂ over Mn²⁺-exchanged zeolites

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ABSTRACT

The Mn²⁺-exchanged zeolites Mn-Y, Mn-beta, Mn-A and Mn-ZSM-5 were prepared and used as heterogeneous catalysts for the liquid phase epoxidation of alkenes with aqueous hydrogen peroxide (30% H₂O₂) at 273–298 K in the NaHCO₃ buffer system. The structures of catalysts were characterized by powder X-ray diffraction (XRD), UV-vis, ICP, BET and IR techniques. Mn-beta and Mn-Y exhibited the best recyclable activity for the epoxidation of styrene to achieve styrene conversions higher than 96.0 and 98.5 mol%, respectively. Mn-beta showed higher activity for cyclohexene and norbornene but lower activity for α -methylstyrene, cinnamyl chloride, indene, cyclooctene and α -pinene than Mn-Y, which could be correlated with the difference of their pore sizes. However, these catalysts did not show any activity for the epoxidation of 1-octene with H₂O₂, possibly due to low electron density of double bonds of linear terminal alkenes.

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1. Introduction

The catalytic epoxidation of alkenes has been a subject of growing interest in the fundamental chemistry and modern industrial processes, since epoxides are key building blocks in organic synthesis [1]. Moreover, epoxide compounds are commercially important intermediates used in the synthesis of products such as chiral pharmaceuticals, pesticides, epoxy paints [2], agrochemicals, perfume materials and sweeteners [3]. Traditionally, epoxides are produced by the epoxidation of alkenes with stoichiometric amount of peracid as oxidant [4]. However, peracid is very expensive, hazardous, and the acid waste converted from the peracid is environmentally undesirable. In order to overcome these disadvantages, organic peroxides [5], hydrogen peroxide (H₂O₂), molecular oxygen and air [6,7] were used as the oxidizing agents for the epoxidation of alkenes. Among these oxygen donors, H₂O₂ is an important oxidant with respect to environmentally cleanness and economic consideration.

Ti-containing zeolites, such as TS-1 [8,9], Ti-beta [10], Ti-MWW [11] and Ti-MCM-41 [12–15], exhibit high activity and selectivity in the epoxidation of alkenes by using H₂O₂ as oxidant; however, these kinds of catalysts are very expensive for extensive applications. Recently, manganese complexes, such as porphyrin-Mn, salen-Mn, phthalocyanin-Mn and triazamacrocyclic-Mn, have been attracting considerable attention due to their cheapness, less-toxicity and high activity for the selective epoxidation of olefins

[16–19]. Porphyrin-Mn and salen-Mn-complexes are regarded as two important homogenous catalysts. In addition, manganese complexes coordinated with simple tetradentate Schiff-base ligands were also applied in the catalytic epoxidation of styrene under mild condition [17].

However, the preparation of Mn-complexes was generally complicated. Lane et al. used MnSO₄ as the catalyst with H₂O₂ in the bicarbonate solutions to detect the epoxidation of alkenes by free Mn²⁺ ions [20–22]. As expected, the simple MnSO₄ catalyst showed considerable activity for the epoxidation, but the catalytic system needed lots of solvent and hydrogen peroxide (H₂O₂/alkene = 10). Recently, mesoporous catalysts (Zr-) Mn-MCM-41 and Mn-SBA-15 were reported to be active for the epoxidation of *trans*-stilbene and styrene with TBHP under mild conditions but almost inactive when H₂O₂ was used as oxidant [23–25]. Very recently, Pescarmona et al. reported that transition-metal-free microporous and mesoporous materials Al-MCM-41, Ga-MCM-41, USY, beta, AlPO-5 and VPI-5 could heterogeneously catalyze the epoxidation of cyclooctene with 50% H₂O₂ in the liquid phase [26,27]. Ga-MCM-41 displayed higher epoxidation activity with all tested alkenes than other catalysts. It is noteworthy that the above systems contained two main defects, i.e. highly concentrated H₂O₂ (50%) or excess amount of oxidant (H₂O₂/alkene molar ratio = 10) was required.

In the present study, a simple ion-exchange method was applied to prepare a series of Mn²⁺-exchanged microporous zeolite catalysts Mn-beta, Mn-Y, Mn-ZSM-5 and Mn-A for the epoxidation of alkenes with 30% H₂O₂ in sodium hydrocarbonate solution. Under the experimental conditions (273–298 K, H₂O₂/alkene \leq 3), Mn-beta and Mn-Y exhibited highly recyclable activity for the selective epoxidation of alkenes with 30% H₂O₂.

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2. Experimental

2.1. Materials

The main materials used in the experiments included commercial molecular sieves (Na-Y, Na-ZSM-5, Na-beta, Na-4A, aerosil-200 (99%, Degussa), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (>99%), $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.5%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>99%) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.5%). The freshly distilled reagents were *N,N'*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMA), methanol, ethanol, ethyl ether, acetonitrile, acetone, *tert*-butyl alcohol and dichloromethane. Other reagents included various alkenes (including styrene, α -methylstyrene, indene, cyclohexene, norbornene, cyclooctene, α -pinene, cinnamyl chloride, and 1-octene), sodium hydrocarbonate solution, aqueous *tert*-butyl hydroperoxide (TBHP, >65%), aqueous NaClO (10.8%), H_2O_2 (30%), and distilled water.

2.2. Preparation of catalysts

Typically, 5.0 g of zeolites (Na-Y, Na-beta, Na-ZSM-5, Na-4A) were added into the aqueous solution (250 ml) of Mn^{2+} salts and stirred at 363 K for 9–10 h. Then solid samples were recovered by filtration, washing with distilled water several times until free Mn^{2+} ions were removed, and drying at 393 K for 5 h. The resultant samples were named Mn-Y, Mn-beta, Mn-ZSM-5, and Mn-A, respectively. For the purpose of comparison, a similar process to the synthesis of Mn^{2+} -exchanged zeolites was used for the preparation of Cu^{2+} , Cr^{3+} , Ni^{2+} -exchanged beta, which were named Cu-beta, Cr-beta, and Ni-beta, respectively. Additionally, $\text{MnO}_x/\text{SiO}_2$ was also prepared by the conventional impregnation method. Typically, an appropriate amount of fumed silica was added to the aqueous solution of $\text{Mn}(\text{NO}_3)_2$ the mixture was stirred for 12 h at ambient temperature, and then excess water was evaporated off at 363 K, followed by drying at 393 K overnight, or calcination at 823 K for 8 h in air.

2.3. Characterization of catalysts

Powder X-ray diffraction (XRD) was recorded on a Rigaku D/MAX-IIIIC diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.54184 \text{ \AA}$) operating at 30 kV and 25 mA. Infrared (IR) spectra were recorded on a Shimadzu IR Prestige-21 Fourier transform infrared spectrophotometer. UV-vis spectra were collected on a Shimadzu UV-visible UV-2550 spectrometer. Autosorb-1 was used to measure the N_2 adsorption-desorption isotherms of the samples, which were degassed at 573 K overnight prior to the measurements. The BET specific surface area was calculated using the BET equation in the relative pressure (p/p_0) range from 0.05 to 0.25. The average crystal sizes were estimated from SEM images, which were observed using a KYKY-1000B scanning electron microscope (SEM) operating at an accelerating voltage of 25 kV and a tube current of 100 μA under vacuum at 10^{-6} mbar. The content of metals in the sample was determined by the inductively coupled plasma (ICP) technique.

2.4. Epoxidation of alkenes

Generally, 100 mg of catalyst and 4.0 mmol of alkene were added to 4.0 ml of DMF in a 25-ml round-bottom flask and the mixture was stirred at 273 K (or 298 K) for 10 min. Then the mixture of 12.0 mmol 30% H_2O_2 (or NaClO, TBHP) and NaHCO_3 (0.2 M, 4 ml) solution was dripped into the above solution within 0.5 h under continuous stirring. Four hours later, the reaction was terminated and the solid catalyst was filtered off. The liquid reaction mixture was extracted by ethyl ether and then quantitatively analyzed by GC-900A equipped with an FID detector and an SE-30 column

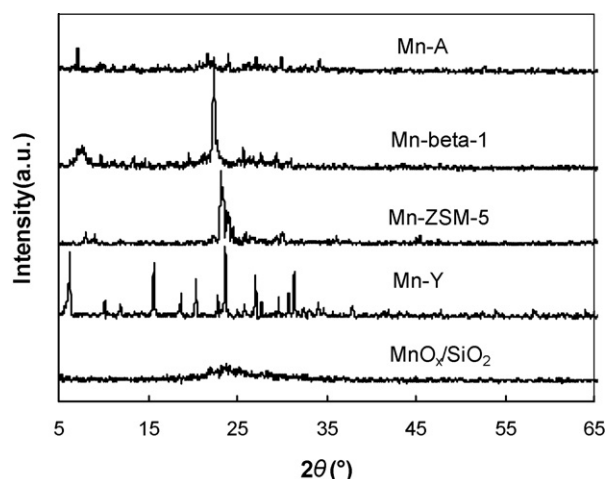


Fig. 1. XRD patterns of (a) Mn-A, (b) Mn-beta-1, (c) Mn-ZSM-5, (d) Mn-Y, and (e) $\text{MnO}_x/\text{SiO}_2$.

($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). Hydrogen was used as carrier gas. GC error for the determination was within $\pm 3\%$. Chlorobenzene was used as internal standard to quantify the components. The conversion of alkene (mol%) was calculated based on the moles of alkene converted to epoxide and other oxidized products. The selectivity of epoxide (%) was the molar ratio of epoxide yielded to alkene converted. Turnover number (TON) equaled the molar ratio of epoxide yielded to manganese metal. In order to investigate the stability and recyclability of the catalysts, the ion-exchanged zeolite was recovered from reaction mixture by filtration, washed with distilled water and ethyl ether repeatedly, dried at 373 K for 6 h, and reused for the next run.

3. Results and discussion

3.1. Structures of catalysts

The XRD patterns of Mn^{2+} -exchanged zeolites (Fig. 1) indicate that the framework structures of zeolites remain intact after the ion-exchange process except for Mn-A. This is because the introduction of Mn^{2+} into zeolite A has a considerable effect on the framework of zeolite A and decreases the Al content in framework. The XRD pattern of $\text{MnO}_x/\text{SiO}_2$ merely displays a broad peak in the range of $15\text{--}35^\circ$. The IR vibrational spectra of Mn-zeolites further proved the integrity of frameworks of the samples that had undergone ion-exchange treatments.

Fig. 2 shows UV-vis spectra of all the catalyst samples. Mn^{2+} -exchanged zeolites exhibit resolved absorbance maxima at ca. 255 nm, similarly to the results reported by the literature [28,29], in which the band around 255 nm was assigned to the $\text{O}^{2-} \rightarrow \text{Mn}^{2+}$ charge-transfer transition. Distinctly, UV-vis/DRS results suggest that the Mn element is present mostly as Mn^{2+} in ion-exchanged zeolites. $\text{MnO}_x/\text{SiO}_2$ contains a band at 255 nm and two broad bands in the region 270–320, 390–430 nm, which could be assigned to the $\text{O}^{2-} \rightarrow \text{Mn}^{2+}$ and the $\text{O}^{2-} \rightarrow \text{Mn}^{3+}$ charge-transfer transition superimposed on ${}^5\text{B}_{1g} \rightarrow {}^5\text{B}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ crystal field *d-d* transitions, respectively [30].

BET surface areas and pore volumes of various zeolites obtained by the BET analysis were $406.5 \text{ m}^2/\text{g}$ and $0.22 \text{ cm}^3/\text{g}$ for Na-ZSM-5, $821.3 \text{ m}^2/\text{g}$ and $0.43 \text{ cm}^3/\text{g}$ for Na-Y, $510.2 \text{ m}^2/\text{g}$ and $0.27 \text{ cm}^3/\text{g}$ for Na-beta, and $155.7 \text{ m}^2/\text{g}$ and $0.15 \text{ cm}^3/\text{g}$ for Na-4A. The average crystal size observed by SEM was 0.5–1.2 μm for Na-ZSM-5, 0.5–2.0 μm for Na-Y, 0.3–1.0 μm for Na-beta, and 0.4–1.1 μm for Na-4A. Mn contents, BET surface areas and Si/Al ratios of Mn-zeolites are also shown in Table 1.

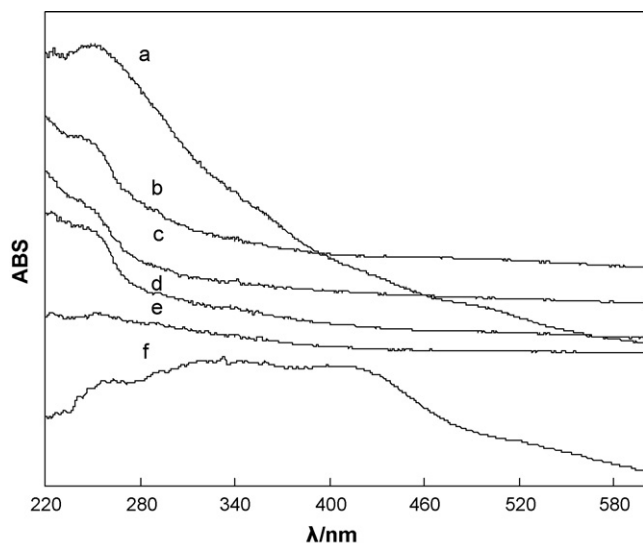


Fig. 2. UV-vis spectra of (a) Mn-A, (b) Mn-beta-1, (c) Mn-beta-2, (d) Mn-ZSM-5, (e) Mn-Y, and (f) $\text{MnO}_x/\text{SiO}_2$.

3.2. Catalytic epoxidation of styrene with 30% H_2O_2

3.2.1. Effect of different catalysts and oxidants

The catalytic properties of various catalysts for the epoxidation of styrene with 30% H_2O_2 are demonstrated in Table 2. Under our experimental conditions, different catalysts with similar Mn contents showed great difference in the catalytic conversion of styrene. MnSO_4 and $\text{Mn}(\text{NO}_3)_2$ catalyzed 28.7 and 30.2 mol% conversions of styrene, respectively, notably lower than 71.5 mol% conversion

obtained by using Mn-ZSM-5 as the catalyst. For the zeolite catalysts containing similar Mn contents, Mn-A achieved a relatively high conversion of styrene up to 98.5 mol%, remarkably higher than those of MnSO_4 and Mn-ZSM-5, but slightly lower than 99.8 mol% of Mn-Y and ca. 100 mol% of Mn-beta-1. When the Mn content in Mn-beta was decreased from 2.4 to 1.2 wt%, the conversion of substrate slightly reduced to 96.4 mol%. However, the epoxide selectivity on these catalysts was high, e.g. 96.4% for MnSO_4 , 95.7% for Mn-ZSM-5 and Mn-A, 96.7% for Mn-Y, and 95.3–96.9% for Mn-beta-1 and Mn-beta-2. As shown in Table 2, the sample (entry 8) dried merely at 393 K overnight but uncalcined converted 39.2 mol% of styrene with 92.6% selectivity of epoxide; however, once calcined at 823 K the epoxidation activity of the resulting sample (entry 9) was notably reduced to 17.8 mol% of styrene conversion with 84.4% selectivity of epoxide, further indicating the importance of Mn^{2+} ions in the epoxidation. The pore diameters or apertures of zeolites are about 7.4 Å for Y, 6.7 Å for beta, 5.4 Å for ZSM-5 and 4 Å for 4A, respectively. However, the catalytic activity of Mn^{2+} -exchanged zeolites cannot be correlated with their pore sizes, which may mean that so long as the active sites of Mn^{2+} ions exposed are sufficient, the epoxidation of styrene can happen readily.

Very clearly, Mn-Y and Mn-beta-1 were the most active, achieving 96.5 and 96.9% of the epoxide yield within 4 h, slightly higher than 94.3% on Mn-A and 91.9% on Mn-beta-2, notably larger than 68.4% on Mn-ZSM-5, 27.7% on MnSO_4 and 28.0% on $\text{Mn}(\text{NO}_3)_2$, which meant the lowest catalytic activity of simple MnSO_4 and $\text{Mn}(\text{NO}_3)_2$ salts in the present reaction as well. Especially, the TON value characterizing the activity of metal ions decreased gradually in the sequence of Mn-beta-2 (168.4) > Mn-beta-1 (88.8) > Mn-Y (84.8) > Mn-ZSM-5 (75.2) \approx Mn-A (74.0) > MnSO_4 (26.8) > $\text{Mn}(\text{NO}_3)_2$ (21.1), which revealed excellent catalytic activity of highly dispersed Mn^{2+} ions. To compare the difference in the catalytic activity between Mn-beta-1 and Mn-beta-2 in the

Table 1

Physicochemical characterization of Mn-zeolite catalysts.

Catalysts	Mn content ^a (wt%)	Parent zeolites ^a Si/Al	Mn-zeolites ^a Si/Al	Surface area ^b (m^2/g)
Mn-beta-1	2.4	25.0	30.6	482.5
Mn-beta-2	1.2	25.0	27.8	496.3
Mn-Y	2.5	4.7	6.7	744.1
Mn-A	2.8	2.2	3.0	123.4
Mn-ZSM-5	2.1	25.0	27.5	397.5

^a Results obtained from ICP-AES.

^b Values obtained from N_2 adsorption results.

Table 2

Effect of various catalysts on the epoxidation of styrene^a.

Run	Catalyst	H_2O_2 efficiency (%)	Styrene conv. (mol%)	Selectivity (%)		Epoxide yield (%)	TON
				Styrene oxide	Benzaldehyde		
1	Mn-ZSM-5	23.8	71.5	95.7	4.3	68.4	75.2
2	Mn-A	32.8	98.5	95.7	4.3	94.3	74
3	Mn-Y	33.3	99.8	96.7	3.3	96.5	84.8
4	Mn-beta-1	33.3	100	96.9	3.1	96.9	88.8
5	Mn-beta-2	32.1	96.4	95.3	4.7	91.9	168.4
6	$\text{Mn}(\text{NO}_3)_2^b$	10.1	30.2	94.4	5.6	28.0	21.1
7	MnSO_4^c	9.6	28.7	96.4	3.6	27.7	26.8
8	$\text{MnO}_x/\text{SiO}_2^d$	13.1	39.2	92.6	7.4	36.3	24.7
9	$\text{MnO}_x/\text{SiO}_2^e$	5.9	17.8	84.4	15.6	15.0	10.2
10	Cu-beta	0.6	1.7	100	0	1.7	1.6
11	Ni-beta	0.7	2.2	100	0	2.2	2.7
12	Cr-beta	0	0	0	0	0	0
13	Na-beta	0	0	0	0	0	0
14	Na-Y	0	0	0	0	0	0

^a Reaction conditions: catalyst (100 mg), DMF (4.0 g), styrene (4 mmol), NaHCO_3 (0.2 M, 4 ml), H_2O_2 (12 mmol), tempt. = 273 K, time = 4 h.

^b 10 mg of $\text{Mn}(\text{NO}_3)_2$ was added.

^c 7 mg of MnSO_4 was added.

^d Dried at 393 K overnight but uncalcined at 823 K.

^e Dried at 393 K overnight and calcined at 823 K.

Table 3
Effect of various oxidants on the epoxidation of styrene catalyzed by Mn-beta-1^a.

Oxidant	Styrene conv. (mol%)	Selectivity (%)			Epoxide yield (%)
		Styrene oxide	Benzaldehyde	Others	
TBHP ^b	18.4	1.4	98.5	0.1	0.26
NaClO ^b	9.1	25.8	1.7	72.5	2.35
H ₂ O ₂ ^b	100	96.9	3.1	0	96.9
Air ^c	–	–	–	–	–

^a Reaction conditions: catalyst (100 mg), DMF (4.0 g), styrene (4 mmol), NaHCO₃ (0.2 M, 4 ml), tempt. = 273 K, time = 4 h.

^b 12 mmol.

^c Flow rate of air (30 ml/min), tempt. = 333 K.

initial kinetic period, the epoxidation reactions with both catalysts were run for only 0.5 h. Thus, the obtained conversions were 32.0 and 21.6 mol%, respectively, in which the TON values of both catalysts in 0.5 h could be calculated at 28.4 and 34.8, obviously showing the higher activity of Mn-beta-2 than Mn-beta-1. Several other transition-metal ions exchanged beta zeolites, such as Cu-beta, Cr-beta and Ni-beta, were also prepared and applied in the epoxidation of styrene. Compared with Mn²⁺-exchanged zeolites, Cu-beta and Ni-beta exhibited extremely low catalytic activities, i.e. 1.7–2.2 mol% of substrate conversions with almost 100% selectivity of styrene oxide; Cr-beta was totally inactive.

Various oxidants including TBHP, H₂O₂, and NaClO were tested to epoxidize styrene over Mn-beta-1 at 273 K. Compared with H₂O₂, both NaClO and TBHP were less efficient for the epoxidation of styrene under the present experimental conditions (Table 3). TBHP as the oxidant converted 18.4 mol% of styrene with only 1.4% selectivity of epoxide and 98.5% of cleaved product benzaldehyde, while NaClO achieved a conversion of only 9.1 mol% and about 25.8% selectivity of epoxide. When only air was introduced into the reaction mixture, no oxidation occurred below 333 K.

3.2.2. Effect of various buffer systems and solvents

Fig. 3 depicts the effect of different concentrations of NaHCO₃ on the epoxidation of styrene at 273 K. The addition of hydrocarbonate was quite effective for the epoxidation reaction catalyzed by Mn-beta, and no reaction occurred without adding NaHCO₃ to the reaction system. When the concentration of NaHCO₃ was increased from 0.05 to 0.2 M, the yield of styrene oxide showed a gradual increase from 47.2 to 96.9%; however, along with a continuous increase of the NaHCO₃ concentration from 0.2 to 1.5 M, the yield of styrene oxide stepwise decreased to 38.1%. The pH value becomes

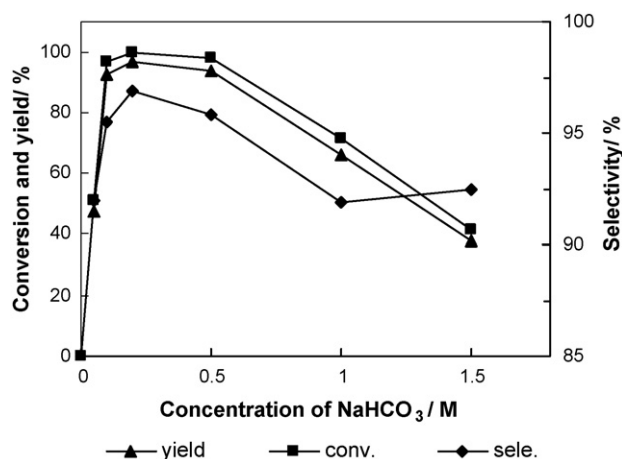
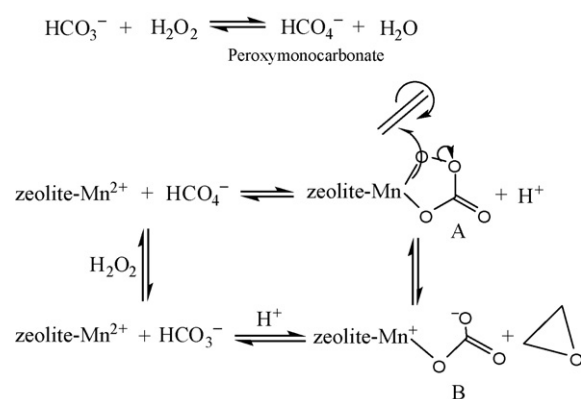


Fig. 3. Effect of concentration of NaHCO₃ on the catalytic performances over Mn-beta-1 catalysts.



Scheme 1. Possible pathway of selective epoxidation of alkene.

larger with the increase in the HCO₃⁻ concentration, so that the deprotonation and decomposition of HCO₄⁻ to CO₃²⁻ becomes significant at pH values above 8–9. Thus, the concentration of HCO₄⁻ will gradually decrease with the increase in the HCO₃⁻ concentration. Consequently, the yield of epoxides will decrease at elevated pH values, because peroxymonocarbonate plays a key role in the catalytic epoxidation circulation as illustrated in Scheme 1. Similar results have been as well reported in the literature [19]. Thus, the optimal concentration of NaHCO₃ solution as the buffer system was 0.2 M. However, when K₂CO₃, Na₂CO₃, NaAc or NH₄Ac was used as the buffer solution, only a trace amount of epoxide was yielded.

Further investigations have also shown the importance of a suitable solvent for titled epoxidation reactions (Table 4). The use of methanol, dichloromethane, ethanol, acetone or *tert*-butyl alcohol as the solvent led to little or no product detected, while using DMF or DMA as the solvent produced high yields of styrene oxide. For these solvents, the yield of epoxide could be arranged in the following order: acetone (2.9%) ≈ acetonitrile (3.2%) < *tert*-butyl alcohol (12.1%) < DMA (70.1%) < DMF (96.9%), inconsistent with the rising order of the solvent polarity, in which DMF was an optimal option.

Since not any styrene could be converted on Na-Y or Na-beta, it is believable that Mn²⁺ ions on zeolites played important roles in the epoxidation. Based on our investigations, a possible reaction mechanism is proposed in Scheme 1, where peroxymonocarbonate ion, HCO₄⁻, is an essential component in this system and more nucleophilic than H₂O₂. Such equilibrium was previously observed by Richardson et al. in the solution of H₂O₂ and bicarbonate in other solvents [31,32]. Then, peroxymonocarbonate ion could coordinate with Mn²⁺ ions on zeolites to form the intermediate A. Subsequently, the intermediate A will transfer active atomic [O] to the double bond of olefinic molecules, forming the epoxide product and B that will quickly decompose into Mn²⁺-zeolite and HCO₃⁻, with which one catalytic circulation is completed. It is noteworthy that epoxidation by hydrocarbonate/H₂O₂ mixtures without any cata-

Table 4
Effect of various solvents on the epoxidation of styrene catalyzed by Mn-beta-1^a.

Solvent	Styrene conv. (mol%)	Selectivity (%)	Epoxide yield (%)
DMF	100	96.9	96.9
DMA	74.3	94.3	70.1
<i>tert</i> -Butyl alcohol ^b	12.1	100	12.1
Acetonitrile	3.2	95.2	3.0
Acetone	2.9	100	2.9
Dichloromethane	0	0	0
Ethanol	0	0	0

^a Reaction conditions: catalyst (100 mg), DMF (4.0 g), styrene (4 mmol), NaHCO₃ (0.2 M, 4 ml), H₂O₂ (12 mmol), tempt. = 273 K, time = 4 h.

^b Tempt. = 298 K.

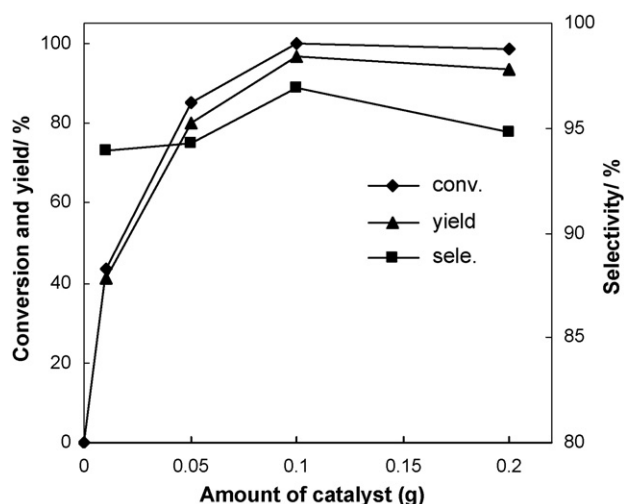


Fig. 4. Effect of catalyst amount on the catalytic performance of styrene over Mn-beta-1 catalysts.

lyst is relatively slow in the solvents used in catalyzed processes, consistent with the observations reported in the literature [21].

3.2.3. Effect of catalyst amount, H_2O_2 /styrene ratio, substrate concentration and reaction time

The effect of the catalyst amount on the conversion and selectivity is illustrated in Fig. 4, where Mn-beta-1 was used as the catalyst. When the amount of Mn-beta-1 was increased from 10 to 100 mg, the conversion of styrene and the selectivity of styrene oxide increased from 41.7 to 100 mol% and from 93.9 to 96.9%, respectively. With a further increase in the catalyst amount from 100 to 200 mg, the conversion of styrene and the selectivity of styrene oxide showed a very small reduction from 100 to 98.5 mol% and from 96.9 to 94.8%, possibly due to trivial decomposition of H_2O_2 and to formation of byproducts promoted by Mn^{2+} ions [1,22].

Fig. 5 describes the effect of H_2O_2 /styrene molar ratio on the catalytic activity of styrene. With the increase in the $n(H_2O_2)/n(styrene)$ molar ratio from 0.5:1 to 3:1, the conversion of styrene was speedily increased from 25.5 to 100 mol%, but the selectivity to styrene oxide was slightly decreased from 99.5 to 96.9%, which was assigned to over-oxidation of styrene oxide in the presence of the excess amount of H_2O_2 . When the

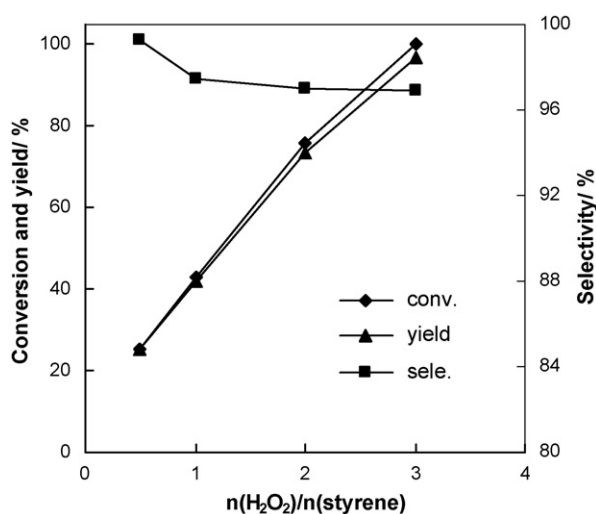


Fig. 5. Effect of H_2O_2 /styrene molar ratio on the catalytic performances of styrene over Mn-beta-1 catalysts.

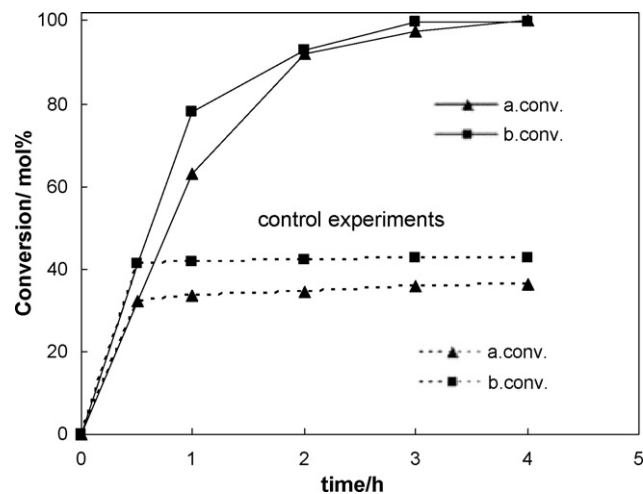


Fig. 6. Effect of reaction time on the catalytic performances over Mn-beta-1 (a) and Mn-Y (b) catalysts.

$n(H_2O_2)/n(styrene)$ was 3:1, the maximal yield of epoxide was attained.

The substrate concentration was another important parameter in the epoxidation of styrene conducted over Mn-beta-1 at 273 K in the medium of DMF and 0.2 M $NaHCO_3$. When the amount of styrene was increased from 2 to 10 mmol, the conversion of styrene stepwise decreased from 100 to 75.8 mol%, accompanied with the decrease in the epoxide selectivity from 97.5 to 88.5%. When the amount of styrene was 4 mmol, the epoxide selectivity reached 96.9%, with a substrate conversion of 100 mol%. A further increase in the styrene amount from 4 to 5 mmol led to rapid decreases in the styrene conversion and the epoxide selectivity to 90.5 mol% and 91.2%, respectively.

We also investigated the effect of reaction time on the epoxidation of styrene over Mn-beta-1 and Mn-Y, as shown in Fig. 6. The epoxide selectivities were 98.2% and 98.3% in 0.5 h, and then slightly reduced to 96.9% and 96.7% in 4 h; however, within the reaction time of 0.5 h, about 32.0 and 41.2 mol% of styrene were respectively converted. With prolonging the reaction time the conversions gradually increased to 100 mol% on Mn-beta-1 and 99.8 mol% on Mn-Y (in 4 h).

3.2.4. Recycling studies

The catalysts Mn-beta-1 and Mn-Y were used for recycling studies. As one can see from Fig. 7, the catalytic activity of Mn-beta-1 catalyst shows an apparent reduction in the initial three recycles, but remains basically unchanged in the following four recycles; however, the catalytic activity of Mn-Y has kept a small fluctuation in the range of 98.5–99.9 mol% conversions in all seven recycles. For Mn-beta-1 the styrene conversion and the epoxide selectivity decreased from 100 to 96.0 mol% and from 96.9 to 93.5% with recycling; however, in the latter four recycles both values maintained more or less constants at ca. 96.0 mol% and 93.6%. For Mn-Y in the latter four recycles the styrene conversion and the epoxide selectivity were kept at higher than 98.5 mol% and 95.5%, respectively. TON values of catalysts are illustrated in Fig. 8. The TON values on Mn-beta-1 and Mn-Y decreased from 88.8 to 82.4 and from 84.8 to 83.3 with recycling, respectively; however, in the latter four recycles both values were kept more or less constant at 82.4 or at 83.3. After being recycled four times, Mn-beta-1 and Mn-Y showed a slight decrease in the Mn contents from 2.4 to 2.1 wt.% and 2.8 to 2.7 wt.%, respectively. Once free Mn^{2+} ions was totally leached out of the pores, no further leaching of Mn^{2+} ions could be detected from the solutions by the ICP analysis. In such catalytic systems, the activity of both catalysts tended to maintain a normal fluctuation

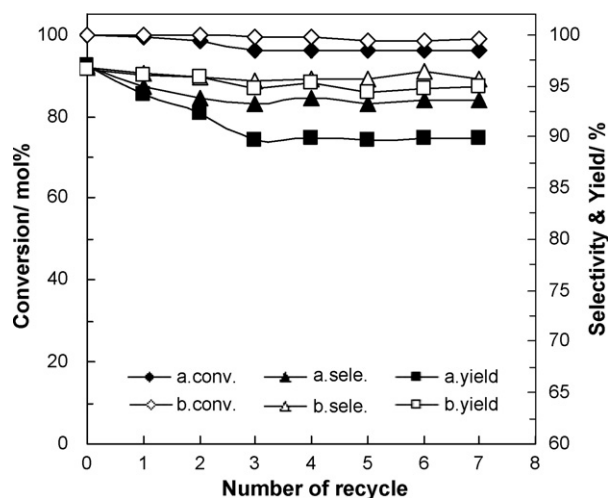


Fig. 7. Recycling studies of catalysts: Mn-beta-1 (solid signs) and Mn-Y (empty signs).

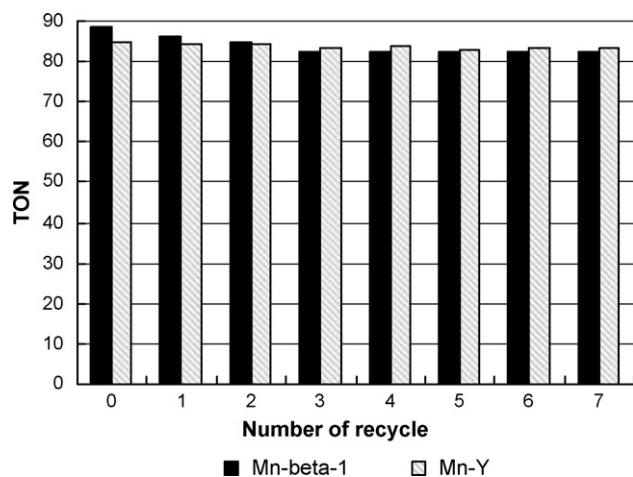


Fig. 8. TON values of Mn-beta-1 and Mn-Y in the recycling studies.

Table 5
Epoxidation of alkenes catalyzed by Mn-beta-1 and Mn-Y^a.

Run	Alkene	Catalyst	Alkene conv. (mol%)	Epoxide selectivity (%)	Epoxide yield (%)
1	Styrene	Mn-beta-1	100	96.9	96.9
		Mn-Y	99.8	96.7	96.5
2	α -Methylstyrene	Mn-beta-1	88.5	90.9	80.4
		Mn-Y	89.2	92.1	82.2
3	Cinnamyl chloride	Mn-beta-1	60.0	85.4	51.2
		Mn-Y	76.8	81.4	62.5
4	Indene	Mn-beta-1	46.0	90.8	41.8
		Mn-Y	63.8	86.8	54.9
5	Cyclohexene	Mn-beta-1	90.7	94.2	85.4
		Mn-Y	84.0	98.2	82.5
6	Norbornene ^b	Mn-beta-1	100	100	100
		Mn-Y	66.1	100	66.1
7	Cyclooctene	Mn-beta-1	13.5	82.9	11.2
		Mn-Y	30.7	91.5	28.1
8	α -Pinene	Mn-beta-1	18.1	88.2	16.0
		Mn-Y	40.1	100	40.1
9	1-Octene	Mn-beta-1	0	0	0
		Mn-Y	0	0	0

^a Reaction conditions: catalyst (100 mg), DMF (4.0 g), alkene (4 mmol), NaHCO₃ (0.2 M, 4 ml), H₂O₂ (12 mmol), tempt. = 273 K, time = 4 h.

^b Tempt. = 298 K.

in an almost constant range. Thus, the small loss in the catalytic activity and selectivity could be assigned to the leaching of free Mn²⁺ species occluded in the pores of zeolites during the reaction process [14].

In order to verify further whether the observed catalysis was truly heterogeneous or not, some control experiments were done according to the method described in the literature [33,34]. The epoxidation of styrene with Mn-beta-1 and Mn-Y was carried out under the same conditions as stated above (273 K). As shown in Fig. 6, when both reactions were initially run for 0.5 h, the obtained conversions were 32.0 and 41.2 mol%, respectively. Subsequently, the solid Mn-zeolite catalysts were filtered off from the reaction mixtures, and the reactions were continued with the resulting filtrates for another 3.5 h. Finally, the conversions on both Mn-beta-1 and Mn-Y were found to be only 36.4 and 42.8 mol% with an extremely low increment of 1.6–4.4 mol% (attributed to the contribution of a trace amount of Mn²⁺ ions leaching from Mn-zeolites), almost equal to the data obtained after 0.5 h but much lower than 100 and 99.8 mol% under the normal reaction mode. This study further revealed the essentiality of heterogeneous catalysis on Mn-beta-1 and Mn-Y.

3.3. Catalytic epoxidation of various alkenes with H₂O₂ over Mn-beta and Mn-Y

Based on the above studies, epoxidations of other eight alkenes were also explored by using Mn-beta-1 and Mn-Y as catalysts (Table 5). In addition to the epoxidation of styrene discussed above in detail, Mn-beta-1 and Mn-Y could catalytically convert 90.7 and 84.0 mol% of cyclohexene to achieve 94.2 or 98.2% selectivity of cyclohexene oxide, respectively; the byproduct was cyclohexene-1-one. For norbornene, Mn-beta-1 was more active than Mn-Y, with 100 and 66.1 mol% conversions, respectively. For cinnamyl chloride, about 60.0 mol% conversion (85.4% selectivity) and 76.8 mol% conversion (81.4% selectivity) were obtained over Mn-beta-1 and Mn-Y, respectively.

However, for the epoxidation of cyclooctene, α -methylstyrene, indene and α -pinene, the catalytic activity of Mn-beta-1 was obviously lower than that of Mn-Y, which could be correlated with the difference in their pore sizes. As shown in Table 5, the yields

of epoxides of various substrates could be ordered as follows: norbornene (100%) > styrene (96.9%) > cyclohexene (85.4%) > α -methylstyrene (80.4%) > cinnamyl chloride (51.2%) > indene (41.8%) > α -pinene (16.0%) > cyclooctene (11.2%) on Mn-beta-1, different from styrene (96.5%) > cyclohexene (82.5%) \approx α -methylstyrene (82.2%) > norbornene (66.1%) > cinnamyl chloride (62.5%) > indene (54.9%) > α -pinene (40.1%) > cyclooctene (28.1%) on Mn-Y. Unfortunately, the epoxidation of 1-octene with H₂O₂ did not occur at all in this catalysis system, possibly due to low π -electron density of linear terminal alkene molecules decreasing the possibility of electrophilic cycloaddition resulting in the epoxidation [27].

4. Conclusions

Several heterogeneous Mn²⁺-zeolite catalysts (the parent zeolites Y, beta, 4A and ZSM-5) were successfully prepared through a traditional ion-exchange procedure. UV-vis and ICP analyses show that Mn²⁺ ions were introduced into the frameworks of zeolites. XRD, BET, and IR data proved that the zeolite frameworks and channels were maintained after the ion-exchange. Among the Mn-/Cu-/Ni-/Cr-exchanged catalysts prepared, Mn-beta and Mn-Y displayed the highest activities for the selective oxidation of styrene to styrene oxide with 30% H₂O₂ as the oxidant in the DMF/NaHCO₃ system at 273 K. Oxidants, solvents and hydrocarbonate exerted great influences on the epoxidation reaction. The yields of epoxides of various substrates can be ordered as follows: norbornene (100%) > styrene (96.9%) > cyclohexene (85.4%) > α -methylstyrene (80.4%) > cinnamyl chloride (51.2%) > indene (41.8%) > α -pinene (16.0%) > cyclooctene (11.2%) on Mn-beta-1, different from styrene (96.5%) > cyclohexene (82.5%) \approx α -methylstyrene (82.2%) > norbornene (66.1%) > cinnamyl chloride (62.5%) > indene (54.9%) > α -pinene (40.1%) > cyclooctene (28.1%) on Mn-Y. The activity of Mn-beta-1 catalyst showed an apparent reduction in the initial three recycles, but remains basically unchanged in the following four recycles; however, that of Mn-Y has kept considerably high conversions of 98.5–99.9 mol% for seven recycles. The small decrease in the catalytic activity could be assigned to the leaching of free Mn²⁺ species occluded in the pores of zeolites during the reaction process.

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